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Excess Thermodynamic Properties of the Ternary System Ethyl Acetate–Ethanol–2-Ethoxyethanol

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The heat of mixing at 48.2 °C was measured for the ternary system ethyl acetate–ethanol–2-ethoxyethanol by using an isothermal phase change calorimeter. The molar excess volumes were computed from density at 40 °C. These data were correlated by the Redlich and Kister equation. The kinematic viscosity was measured at 30, 40, 50, 60, and 70 °C by using an Ostwald viscometer. These were correlated by the Chandramoulli and Laddha equation based on the McAllister model. The heat of mixing was predicted from viscosity data by using excess free energy of flow and the Gibbs–Helmholtz equation.

The excess thermodynamic properties of the ternary mixtures have gained much importance in recent years in connection with the theories of liquid mixtures. These excess properties in turn reflect on the nonideal nature of the solutions. Since these excess properties are due to molecular interactions, they may be helpful in predicting various physical properties. The heat of mixing data are of much importance in design calculations. Viscosities of pure liquids as well as those of liquid mixtures are much needed in engineering and science. Data for ternary systems at various temperatures and compositions are lacking in the literature.

Experimental Procedure

Materials. Ethyl acetate (A.R. grade, B.D.H., India) and 2-ethoxyethanol (A.R. grade, B.D.H. Poole, England) were dried over silica gel overnight and were further purified in a laboratory fractionating column with an effective length of 1 m and with a packing of ceramic insulating beads. The column was run at total reflux for 0.5 h and the low boiling impurities were drawn off at low rate of reject. The overhead product of desired purity (checked for density and refractive index) was collected and stored in colored bottles. The absolute alcohol supplied by Maharashtra Government distillery, Chitali, India, was dried over anhydrous calcium oxide overnight and was further purified as mentioned above. The physical properties of the pure components with their literature values are reported in Table I.

Apparatus.* (*1*) *Calorimeter. The isothermal phase change calorimeter, similar to one described in the literature (*2*, *6*), was used for measurement of ternary heat of mixing. Briefly, the calorimeter consists of a cylindrical Dewar jar accomodating the first test liquid and a sealed thin-walled bulb containing the second test liquid. The vapor space in the calorimeter was kept very small and the hand-driven stirrer was connected with a mercury seal. This jar was surrounded by a thin mantle of dilatometric fluid (cetyl alcohol, mp 48.2 °C). The change in the volume of the dilatometric fluid on phase transformation was communicated to the mercury, whose expansion in a calibrated capillary was measured with a cathetometer to ±0.01 mm. The conventional bulb breaking method for mixing of the two components was adopted. The calorimeter was kept in a thermostat at 48.2 ± 0.1 °C. The instrument was calibrated by Kalasy et al. (*3*) by using the standard neutralization method. Ternary heat of mixing data were obtained by mixing various amounts of 2-ethoxyethanol with mixtures of ethyl acetate and ethanol of varying compositions.

(*2*) *Viscometer.* Viscosity of the ternary mixtures was measured with an Ostwald viscometer, calibrated against double-distilled water at different temperatures. The efflux time was measured by visual observation of the meniscus three times for every reading, agreeing to ±0.5 s by a stopwatch.

(*3*) *Pycnometer.* Excess volume of the ternary mixtures was obtained at 40 ± 0.1 °C from density measurements. A pycnometer of approximately 15–20 mL capacity was used in all of the above determinations.

Results and Discussion

Experimental heat of mixing data at 48.2 °C are given in Table II and plotted in Figure 1 for 20, 40, and 60% of 2-ethoxyethanol in the ternary mixture. These data are endothermic and decrease with an increase in the amount of 2-ethoxyethanol. The data are correlated by the Redlich and Kister equation (*10*).

$$H_{123}^E = x_1x_2[A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] + x_1x_3[A_{13} + B_{13}(x_1 - x_3) + C_{13}(x_1 - x_3)^2] + x_2x_3[A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] + C^*x_1x_2x_3 \qquad (1)$$

The variations of kinematic viscosity with temperature and composition are given in Table III. The viscosity increases with an increase in 2-ethoxyethanol concentration and decreases with an increase in temperature. The data are correlated by the equation

$$\ln \nu_{\text{mix}} = x_1^3 \ln \nu_1M_1 + x_2^3 \ln \nu_2M_2 + x_3^3 \ln \nu_3M_3 + 3x_1^2\left[x_2 \ln \nu_{12} + x_3 \ln \nu_{13} + x_2 \ln \frac{2M_1 + M_2}{3} + x_3 \ln \frac{2M_1 + M_3}{3}\right] + 3x_2^2\left[x_1 \ln \nu_{21} + x_3 \ln \nu_{23} + x_1 \ln \frac{2M_2 + M_1}{3} + x_3 \ln \frac{2M_2 + M_3}{3}\right] + 3x_3^2\left[x_1 \ln \nu_{31} + x_2 \ln \nu_{32} + x_1 \ln \frac{2M_3 + M_1}{3} + x_2 \ln \frac{2M_3 + M_2}{3}\right] + 6x_1x_2x_3\left[\ln \nu_{123} + \ln \frac{M_1 + M_2 + M_3}{3}\right] - \ln (x_1M_1 + x_2M_2 + x_3M_3) \qquad (2)$$

derived by Chandramoulli and Laddha (*1*) based on the McAllister model (*8*). The values of binary and ternary constants used in eq 2 and the root-mean-squares deviations are shown in Table III.

Prediction of Heats of Mixing from Viscosity Data

The various methods of predicting the heat of mixing from viscosity data are given in the literature (*4*, *5*, *9*, *12*). The method of Krishnan and Laddha (*4*) was applied for the present

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Table I. Physical Properties of the Chemicals

components	bp, °C (760 mmHg) exptl	bp, °C (760 mmHg) lit.	density, g/mL (40 °C) exptl	density, g/mL (40 °C) lit.	refractive index (30 °C) exptl	refractive index (30 °C) lit.
ethyl acetate	77.10	77.10 (*11*) 77.114 (*13*)	0.8756	0.8759 (*11*)	1.3687	1.3701 (*11*) 25 °C
ethanol	78.30	78.30 (*13*) 78.32 (*11*)	0.7721	0.7722 (*11*) 0.7720 (*7*)	1.3553	1.3573 (*11*)
2-ethoxyethanol	135.10	135.10 (*11*) 135.10 (*7*)	0.9101	0.9300 (*11*) 25 °C 0.9218 (*13*) 30 °C	1.4025	1.4061 (*13*) 25 °C

Table II

Heats of Mixing of the Ternary System Ethyl Acetate (1)–Ethanol (2)–2-Ethoxyethanol (3)

mole fraction			H_{123}^E, cal/g-mol	
ethyl acetate	ethanol	2-ethoxy-ethanol	exptl	calcd
0.1027	0.6962	0.2011	103.0	
0.2018	0.5969	0.2013	164.4	170.0
0.3017	0.4939	0.2044	202.5	
0.4870	0.3157	0.1973	215.0	225.9
0.6042	0.1936	0.2022	182.4	
0.6964	0.1029	0.2007	153.2	152.1
0.1003	0.4968	0.4029	96.3	
0.2031	0.3952	0.4017	146.5	150.4
0.2945	0.3099	0.3956	178.1	180.2
0.4048	0.1923	0.4029	183.0	182.0
0.5237	0.0979	0.3784	152.0	150.0
0.1025	0.3084	0.5891	95.1	95.3
0.2102	0.1987	0.5901	114.3	116.2
0.3021	0.0961	0.6018	119.0	
0.3524	0.0317	0.6159	116.0	115.7
RMSD			6.7 (eq 1), 4.5 (eq 4)	

Values of Binary and Ternary Constants in Equation 1

$A_{12} = 928.500$ $A_{23} = 77.077$ $A_{31} = 489.640$

$B_{12} = -11.200$ $B_{23} = 0.000$ $B_{31} = 23.500$

$C_{12} = 66.122$ $C_{23} = -8.929$ $C_{31} = 45.714$

$C^* = 343.693$

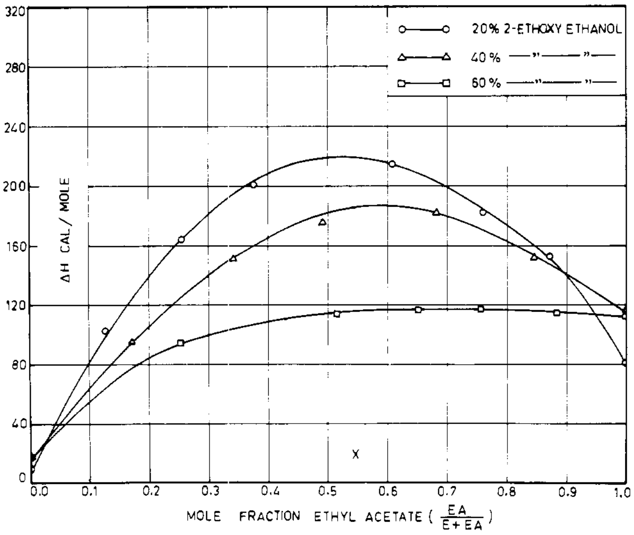

Figure 1. Heats of mixing at 48.2 °C.

experimental data. The excess free energy of flow at different temperatures for 20, 40, and 60% 2-ethoxyethanol were obtained from the equation

$$G_{123}^E/RT = x_1 \ln \nu_1 M_1 + x_2 \ln \nu_2 M_2 + x_3 \ln \nu_3 M_3 - \ln \nu_{mix} - \ln (x_1 M_1 + x_2 M_2 + x_3 M_3) \quad (3)$$

Figure 2 is the plot of G_{123}^E/RT vs. $1/T$ for 20% 2-ethoxyethanol. The heat of mixing data are predicted at different concentrations and at 48.2 °C by using the Gibbs–Helmholtz equation.

$$H^E = [\delta(G^E/T)/\delta(1/T)]_{P,x} \quad (4)$$

Table III

Viscosity Data for the System Ethyl Acetate (1)–Ethanol (2)–Ethoxyethanol (3)

mole fraction			kinematic viscosity (ν), cm^2/s				
ethyl acetate	ethanol	2-ethoxy-ethanol	30 °C	40 °C	50 °C	60 °C	70 °C
0.6974	0.0977	0.2049	0.6084	0.5473	0.4765	0.4381	0.4308
0.6020	0.1972	0.2008	0.6346	0.5631	0.4864	0.4517	0.4394
0.4905	0.3091	0.2004	0.6327	0.6026	0.5221	0.4951	0.4444
0.3031	0.4922	0.2047	0.8367	0.7234	0.6359	0.5693	0.5025
0.2035	0.5941	0.2024	0.9449	0.8319	0.7087	0.6308	0.5533
0.1045	0.6952	0.2003	1.1061	0.9769	0.8704	0.7272	0.6223
0.5276	0.0910	0.3814	0.8021	0.6667	0.6211	0.5433	0.4902
0.3905	0.2021	0.4074	0.9007	0.7040	0.6428	0.5726	0.5071
0.2929	0.3108	0.3963	0.9971	0.8354	0.7296	0.6376	0.5779
0.2055	0.3917	0.4028	1.0961	0.9339	0.8210	0.7012	0.6199
0.1026	0.4961	0.4013	1.2940	1.0814	0.9411	0.8030	0.6948
0.3039	0.1022	0.5939	1.1147	0.9630	0.8466	0.7456	0.6519
0.2084	0.1928	0.5988	1.2498	1.0863	0.9019	0.7961	0.6926
0.1023	0.3127	0.5850	1.4206	1.1994	1.0200	0.8994	0.7621
RMSD			0.0082	0.0040	0.0083	0.0152	0.0072

Values of Binary and Ternary Constants in Equation 2

constants	30 °C	40 °C	50 °C	60 °C	70 °C
ν_{12}	0.5028	0.4582	0.4217	0.3893	0.3628
ν_{21}	0.4961	0.4376	0.3947	0.3551	0.3218
ν_{23}	1.5403	1.2967	1.1630	0.9753	0.8253
ν_{32}	1.4921	1.3304	1.0939	0.9867	0.8251
ν_{13}	0.5481	0.5428	0.6653	0.3845	0.6623
ν_{31}	1.4242	1.0199	1.1125	0.9092	1.0339
ν_{123}	0.0373	0.2660	0.8490	0.2370	1.2807

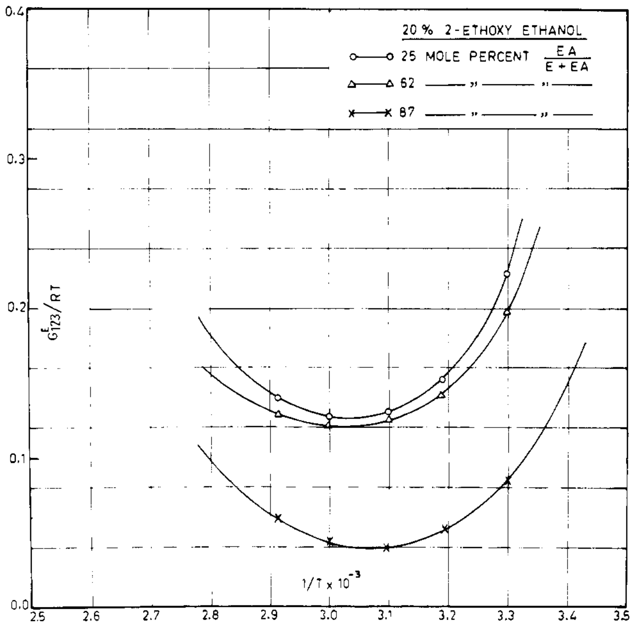

Figure 2. G_{123}^E/RT vs. $1/T$ diagram.

The calculated values of heat of mixing from viscosity data by using eq 4 and the root-mean-squares deviation between the experimental and the calculated values by using eq 1 and 4 are reported in Table II.

Table IV
Excess Volume of Mixing Data for the System Ethyl Acetate (1)-Ethanol (2)-2-Ethoxyethanol (3)

mole fraction			V^E mL/mol
ethyl acetate	ethanol	2-ethoxyethanol	exptl
0.7000	0.1000	0.2000	0.1495
0.2998	0.5002	0.2000	0.0076
0.1000	0.7000	0.2000	0.1096
0.4893	0.3150	0.1957	0.1349
0.5000	0.0999	0.4001	0.1311
0.4000	0.1999	0.4001	0.0887
0.2936	0.3148	0.3961	0.0164
0.2193	0.3880	0.3927	0.0252
0.3000	0.0999	0.6001	0.0058
0.2999	0.1999	0.6001	−0.0668
0.0979	0.3148	0.5873	−0.1621
0.3000	0.0999	0.6001	−0.0058
0.1000	0.0999	0.8001	−0.1224
0.1499	0.0501	0.8000	−0.0344
0.2000	0.0500	0.7500	−0.0618
0.0500	0.1000	0.8500	−0.0930
RMSD			0.0003

Values of Constants in Equation 5

$A_{12} = 3.6500$	$A_{13} = 0.4300$	$A_{23} = -1.0900$
$B_{12} = 0.3629$	$B_{13} = -0.6250$	$B_{23} = -0.3620$
$C_{12} = 0.5880$	$C_{13} = 0.1906$	$C_{23} = -0.1330$
	$C^* = -2.9230$	

Excess volume of mixing at 40 °C was calculated from density data. This is given in Table IV. These data are correlated by eq 5. The values of binary and ternary constants are also given

$$V_{123}{}^E = x_1x_2[A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2] + x_1x_3[A_{13} + B_{13}(x_1 - x_3) + C_{13}(x_1 - x_3)^2] + x_2x_3[A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2] + C^*x_1x_2x_3 \quad (5)$$

in Table IV. The least-squares method was applied for calculating the binary and ternary constants.

Glossary

A, B, C	binary constants in eq 1 and 5
C^*	ternary constant
G^E	excess free energy of mixing, cal/mol
$G_{123}{}^E$	ternary excess free energy of mixing, cal/mol
H^E	heats of mixing, cal/mol
$H_{123}{}^E$	ternary heats of mixing, cal/mol
M	molecular weight
P	system pressure
R	gas constant
RMSD	root mean square deviation, $= [\sum(\nu_{\text{exptl}} - \nu_{\text{calcd}})^2/N]^{1/2}$
N	number of data points
T	absolute temperature, K
$V_{123}{}^E$	ternary molar excess volume, mL/mol
x	mole fraction

Greek Letters

ν	kinematic viscosity, cm²/s
ν_{12}, ν_{23}, ν_{31}	binary constants in eq 2
ν_{123}	ternary constant in eq 2
ν_{mix}	kinematic viscosity of mixture, cm²/s

Subscripts

1, 2, 3	components one, two, and three
exptl	experimental
calcd	calculated
lit.	literature

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Isothermal Vapor–Liquid Equilibria of Allyl Alcohol–Toluene at 90 °C

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Isothermal vapor–liquid equilibria of allyl alcohol–toluene are presented at 90 °C. The system showed positive deviations from Raoult's law and formed an azeotrope at 720 mmHg total pressure with the composition of allyl alcohol at 64 mol %. The system formed a symmetric solution. The activity coefficient data were correlated by the single-parameter Margules equation log $\gamma_i = 0.65(1 - x_i)^2$.

Anhydrous allyl alcohol is obtained by the azeotropic distillation of the constant boiling mixture of allyl alcohol and water. Allyl alcohol and water are formed as reaction products in the manufacture of the former either from allyl chloride by hydrolysis or from acrolein by oxidation. In an attempt to select a suitable entrainer for the azeotropic distillation, toluene was studied for its suitability as a possible entrainer. Earlier the vapor–liquid equilibrium data of allyl alcohol–toluene at 760 mmHg pressure was reported (*1*, *5*). In this work the isothermal vapor–liquid equilibrium data at 90 °C was determined.

Experimental Section

Chemicals. Toluene of analytical grade supplied by B.D.H. (India), Ltd., was further purified in a laboratory distillation column and the fraction boiling at 110.6 °C was collected and used.

Analytical grade allyl alcohol supplied by B.D.H. (India), Ltd., was distilled in a laboratory packed distillation column and the

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